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Synthesis and Characterization of Oligomeric Anilines

by

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The synthesis of well characterized polyaniline oligomers, H-[$(C_6H_4)_n-N(H)$] _n -H ($n=4, 8, 16$) (depicted for simplicity in the fully reduced form) from commercial dianiline, ($n=2$) is reported. Rapid oxidative coupling reactions result predominately in the formation of tetramer, octamer and hexadecamer, respectively, when the reagents are mixed in optimum ratios. Doping by HCl after conversion to the emeraldine oxidation state resulted in conductivities in the range from $\sim 10^{-3}$ to $\sim 10^{-2}$ S/cm.			
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SYNTHESIS AND CHARACTERIZATION OF OLIGOMERIC ANILINES

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Abstract

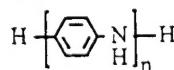
The synthesis of well characterized polyaniline oligomers, $H-[C_6H_4-N(H)]_n-H$ ($n = 4, 8, 16$) (depicted for simplicity in the fully reduced form) from commercial dianiline, ($n = 2$), is reported. Rapid oxidative coupling reactions result predominantly in the formation of tetramer, octamer and hexadecamer, respectively, when the reagents are mixed in optimum ratios. Doping by HCl after conversion to the emeraldine oxidation state resulted in conductivities in the range from $\sim 10^{-3}$ to $\sim 10^{-2}$ S/cm.

Introduction

There is a continually growing interest in conjugated polymers as components of electronic devices based on their *semiconducting* properties. Thin film devices, such as field-effect transistors (1), light-emitting diodes (2) and volatile organic vapor sensors (3), have been fabricated from these conjugated polymers and oligomers. Conjugated oligomers are, in principle, more desirable to study than their corresponding polymer forms since they can be synthesized in the chemically pure state with precisely known molecular weight, molecular conformation, electronic, magnetic and optical properties. They have however, not yet received the attention they deserve except for elegant studies of the sexithiophene oligomer which show that certain of its desirable properties far exceed those of polythiophene (1).

Because of its convenient synthesis and excellent stability in air, polyaniline has become one of the most studied conjugated polymers in the conducting polymer field. A polyaniline tetramer, "azurin", was reported in 1907 without comprehensive analyses (4). In 1968, Honzl (5) reported a series of oligoaniline derivatives. Based on a modified Honzl approach, Wudl et al., (6) synthesized a phenyl-capped octamer which was reported to have essentially the same electronic, electrical and spectroscopic properties as polyaniline.

Polyaniline oligomers may in principle be end-capped with a combination of a variety of groups such as phenyl, amine, etc. (7). We have been particularly interested in oligomers of the type



represented for simplicity in their completely reduced form, capped with a phenyl group at one end and an amine at the other. In this study, we present a general, simple method for the synthesis of parent polyaniline oligomers such as tetramer, octamer and hexadecamer in aqueous solution by oxidative coupling reactions of aniline oligomers in their *reduced* states.

Description of equipment and processes

All chemicals were used as received. N-phenyl-1,4-phenylenediamine (98%), anhydrous hydrazine (98%) and N-methyl-2-pyrrolidinone (NMP) were from Aldrich. Ammonium peroxydisulfate (98%), ferric chloride hexahydrate (99%), ammonium hydroxide (30%), hydrochloric acid (37%), carbon (decolorizing DARCO G-60), diethyl ether (99%), cyclohexane (99%), ethanol (95%), and tetrahydrofuran (99%) (THF) were from Fisher.

Vacuum filtration was carried out with a Buchner funnel with #4 Whatman filter paper by using a water aspirator. GPC experiments were performed in THF solution with a 1.0ml/min flow rate. The GPC column had a linear molecular weight (polystyrene standard) range from 50 to 1500. The column was calibrated by polystyrene standards and aromatic amines.

Synthesis of tetramer

Ferric chloride hexahydrate (0.1mole) was dissolved in 50ml 0.1M HCl at room temperature. N-phenyl-1,4-phenylenediamine (dimer, 0.1mole) was suspended in 2000ml 0.1M HCl in a 4000ml beaker with strong mechanical stirring for 0.5 hour at room temperature. The ferric chloride solution was added to the dimer suspension, with strong stirring, *very quickly*. The suspension was then stirred for 2 hours.

After 2 hours, the suspension was filtered by vacuum filtration. The precipitate was transferred into 500ml of 0.1M HCl. The resulting suspension was stirred for 1 hour, and filtered through the same Buchner funnel. This washing process was repeated 5 times. Alternatively, the precipitate could be separated and washed by centrifugation.

The precipitate was dedoped by 0.1M ammonium hydroxide for 4 hours. The precipitate was dried in a dynamic vacuum for 24 hours at room temperature.

The as-synthesized tetramer was reduced to the leucoemeraldine oxidation state with anhydrous hydrazine in ethanol. After filtration, the powder was treated with carbon black and recrystallized from ethanol.

Synthesis of octamer

Ferric chloride hexahydrate (0.01mole) was dissolved in 15ml 0.1M HCl at room temperature. The tetramer in the leucoemeraldine oxidation state (0.01mole) was suspended in 100ml 0.1M HCl solution with magnetic stirring for 0.5 hour at room temperature. The ferric chloride solution was added *very quickly* to the tetramer suspension with strong stirring. The suspension was then stirred for 2 hours.

After 2 hours, the suspension was filtered by vacuum filtration. The precipitate was transferred into 300ml of 0.1M HCl. The resulting suspension was stirred for 1 hour, and filtered through the same Buchner funnel. This washing process was repeated twice. Alternatively, the precipitate could be separated and washed by centrifugation.

The precipitate was neutralized by stirring in 300ml 0.1M ammonium hydroxide for 5 hours. The precipitate was dried in dynamic vacuum for 24 hours at room temperature. The dried powder was extracted with 250ml of cyclohexane using a Soxhlet extractor. The insoluble powder remaining in the thimble was the octamer. It was held in a desiccator under dynamic vacuum for 24 hours before characterization.

Synthesis of hexadecamer

Ammonium peroxydisulfate (0.015mole) was dissolved in 30ml of 0.1M HCl solution at room temperature. The tetramer in the leucoemeraldine oxidation state (0.01mole) was suspended in 200ml 0.1M HCl solution with magnetic stirring for 0.5 hour at room temperature. The ammonium peroxydisulfate solution was added *very quickly* to the tetramer suspension with vigorous stirring. The suspension was then stirred for 2 hours.

After 2 hours, the suspension was filtered, washed and neutralized following the above method. The dried powder was extracted with 250ml diethyl ether using a Soxhlet extractor. The insoluble powder remaining in the thimble was the hexadecamer. The powder was held in a desiccator under dynamic vacuum for 24 hours before characterization.

Presentation of data and results

Analysis results for tetramer

A typical elemental analysis for *as-synthesized* (emeraldine) tetramer $C_{24}H_{20}N_4$ was: Found, C, 78.81, H, 5.60, N, 15.27, total: 99.68%. Calcd, C, 79.10, H, 5.53, N, 15.37. Its mass spectrum showed a (molecular parent

ion +1) peak at 365 (MH^+/ϵ) by chemical ionization (CI) as shown in Figure 1(A). Its molecular weight by GPC (polystyrene and aromatic amine standards) was 374 shown in Figure 2(A). The as-synthesized tetramer (emeraldine) has an "exciton" peak at 588nm in NMP as shown in Figure 3(A). The diffuse reflectance FTIR spectra is given in Figure 4(A).

The tetramer powder in the emeraldine oxidation state was suspended in 500ml 1M HCl for 24 hours at room temperature. The doped powder was collected by vacuum filtration and was dried under dynamic vacuum for 20 hours at room temperature. The conductivity of the HCl-doped tetramer was 3.0×10^{-3} S/cm (compressed pellet, 4 probe).

A typical elemental analysis for the tetramer in the leucoemeraldine oxidation state: $C_{24}H_{22}N_4$ was: Found, C, 78.38, H, 6.02, N, 15.28, total, 99.68%. Calcd, C, 78.68, H, 6.05, N, 15.29. The mass spectrum showed a (molecular parent ion +1) peak at 367 (MH^+/ϵ) by chemical ionization (CI) as in Figure 1(B). 1H NMR (DMSO): 7.7(s,1), 7.5(s,1), 7.2(s,1), 7.1(t,2), 6.8(m,12), 6.6(t,1), 6.5(d,2) and 4.6(s,2). ^{13}C NMR (DMSO): 145.7, 142.6, 139.9, 139.8, 135.1, 134.1, 133.5, 129.0, 121.0, 120.5, 119.6, 117.7, 116.3, 115.9, 114.9 and 114.4 (TMS std.). These data are in agreement with the proposed structure.

Analysis results for octamer

Elemental analysis for *as-synthesized* octamer (emeraldine) $C_{48}H_{38}N_8$ was: Found, C, 78.03, H, 5.72, N, 14.89, total, 98.64%. Calcd, C, 79.32, H, 5.27, N, 15.42. Its mass spectrum showed a (molecular parent ion +1) peak at 727 (MH^+/ϵ) by laser desorption ionization (LDI) as shown in Figure 1(C). Its molecular weight by GPC (polystyrene and aromatic amine standards) was 743 as shown in Figure 2(B). The "exciton" peak of *as-synthesized* octamer in NMP is present at 599 nm as shown in Figure 3(B).

The octamer powder in the emeraldine oxidation state was suspended in 500ml 1M HCl for 24 hours at room temperature. The doped powder was collected by vacuum filtration and was dried under dynamic vacuum for 20 hours at room temperature. The conductivity of the HCl-doped octamer was 1.7×10^{-2} S/cm (compressed pellet, 4 probe).

Analysis results for hexadecamer

The mass spectrum showed a (molecular parent ion +1) peak at 1451 (MH^+/ϵ) by laser desorption ionization in Figure 1(D). The molecular weight by GPC (polystyrene and aromatic amine standards) was 1486 as in Figure 2(C). The "exciton" peak of *as-synthesized* hexadecamer in NMP was 610 nm (Figure 3C), compared with its value of 638nm in polyaniline (EB) (Figure 3D). The diffuse reflectance FTIR spectrum was shown in Figure 4(B).

The as-synthesized hexadecamer (0.5g) was suspended in 500ml 1M HCl for 24 hours at room temperature. The doped powder was collected by vacuum filtration and was dried under dynamic vacuum for 24 hours at room temperature. The conductivity of HCl-doped hexadecamer was 4.0×10^{-3} S/cm (compressed pellet, 4 probe).

Interpretation of data

The oxidation potential of aniline is higher than that of dianiline and that of dianiline is higher than that of the tetramer. Hence, the ease of oxidation of anilines is expected to increase on proceeding towards higher oligomers of anilines.

Polyaniline is synthesized by a relatively slow oxidative coupling reaction of aniline in acidic aqueous solution. It is therefore to be expected that as soon as dianiline is formed in the oxidative polymerization of aniline that it would undergo further oxidative coupling in preference to aniline. Hence, the final degree of polymerization would be controlled by the relative proportion of oxidant, the oxidant being consumed primarily in oxidizing the (higher) oligomers rather than in slowly oxidizing the aniline. This conclusion also assumes that the oxidant is consumed preferentially in oxidative coupling reactions rather than in the oxidation of already-formed oligomeric or polymeric anilines to higher oxidation states (e.g., permigraniline oxidation state) of an already synthesized molecule.

Since dianiline is oxidized much more rapidly than aniline, rapid mixing of dianiline and oxidant in the correct molar proportion needed for the synthesis of a given oligomer would be expected to result primarily in the preferred formation of the desired oligomer. This has been confirmed experimentally in this study.

We have shown that the octamer and hexadecamer synthesized by the above procedure are in the emeraldine oxidation state as described below. Each oligomer was first reduced by N_2H_4 to the leucoemeraldine oxidation state and was then controllably re-oxidized by the addition of H_2O_2 , its Vis/UV spectrum being constantly monitored (see Figures 5 and 6). In each case, the "exciton" peak grew in intensity at its characteristic λ_{max} until finally, on a further addition of H_2O_2 , it started to undergo a blue shift. This showed that the emeraldine oxidation state had been reached and just exceeded to form a more highly-oxidized molecule (8,9). The λ_{max} recorded just before the blue shift started, is taken as representing the spectrum of the emeraldine oxidation state, as can be seen in comparing the λ_{max} values given in Figure 3.

The conductivities of the aqueous HCl-doped oligomers range from 10^{-3} to 10^{-2} S/cm, which is two or three orders of magnitude lower than that of polymer. This offers the opportunity of directly studying the relative importance of *intra-molecular* and *inter-molecular* contributions to the bulk conductivity of polyaniline.

Conclusions

A general method is described for the synthesis of parent oligomers of polyaniline in aqueous solution by oxidative coupling reactions. The tetramer, octamer and hexadecamer have been well characterized. The as-synthesized oligomers are in the emeraldine oxidation state. The conductivities of the doped oligomers were two or three orders of magnitude lower than that of doped polyaniline (~ 3 S/cm).

Acknowledgments

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Keywords

Oligomeric anilines, Oxidative coupling, Oxidation state and Characterization.

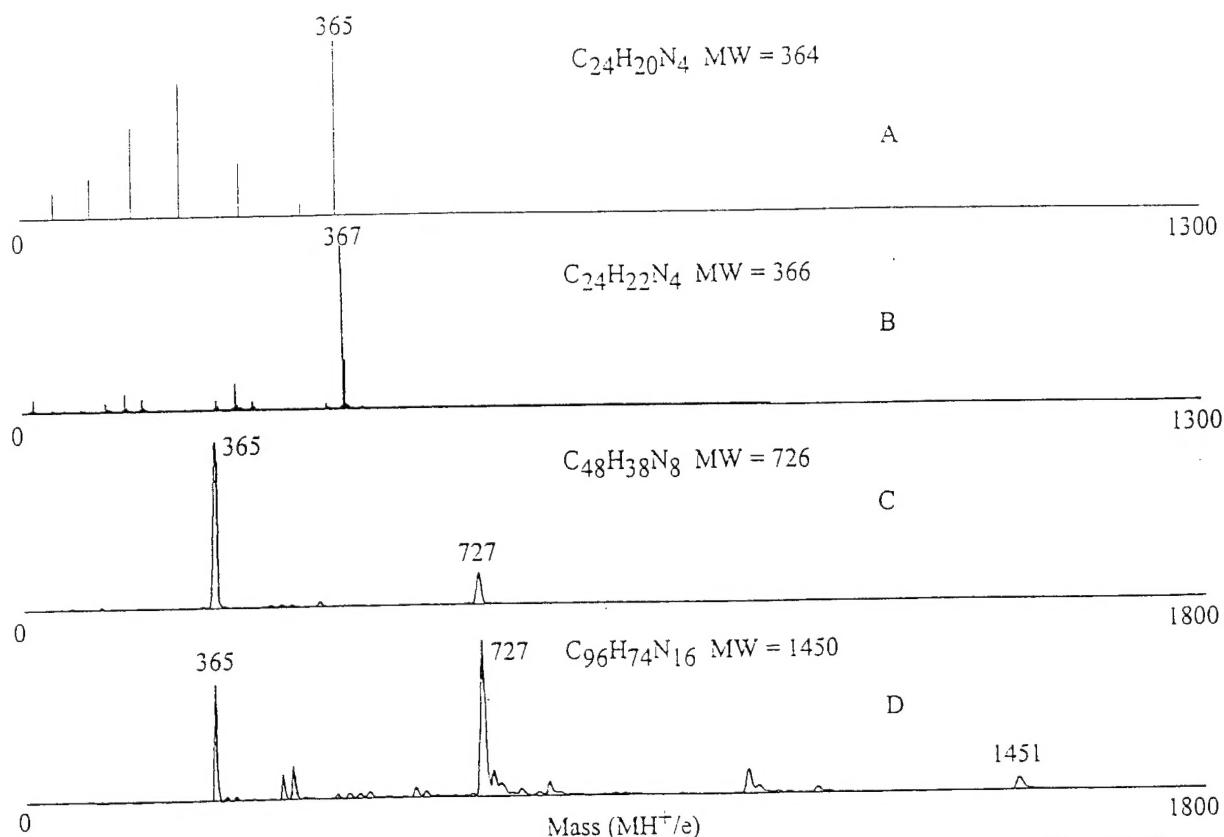


Figure 1. Mass spectra of oligomeric anilines, (A) as-synthesized (emeraldine state) tetramer (CI); (B) Tetramer in leucoemeraldine state (CI); (C) as-synthesized (emeraldine state) octamer (LDI); (D) as-synthesized (emeraldine state) hexadecamer (LDI)

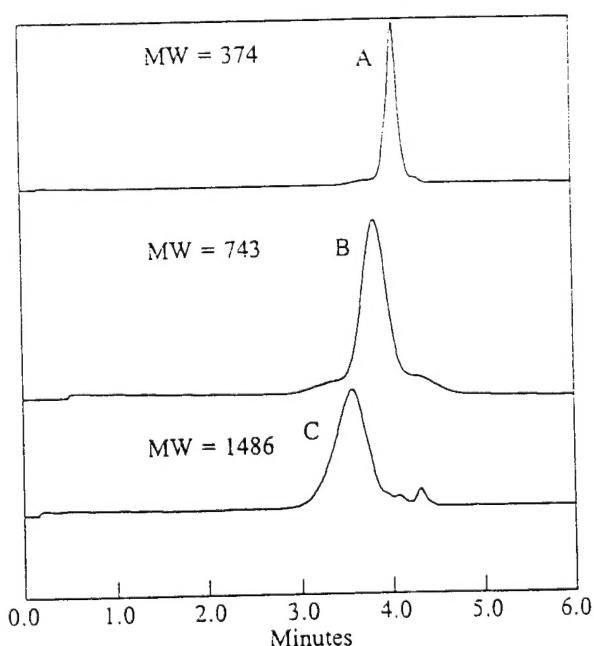


Figure 2. GPC profiles of oligomeric anilines in THF calibrated by polystyrene standards and aromatic amines. (A) as-synthesized tetramer; (B) as-synthesized octamer; (C) as-synthesized hexadecamer, (all in emeraldine state)

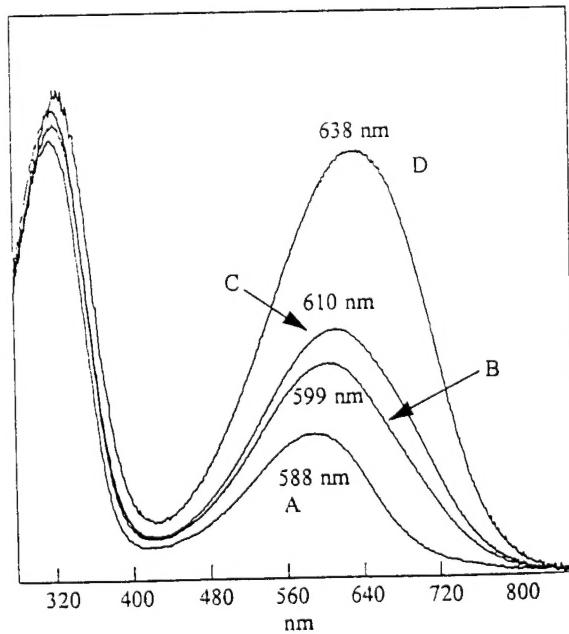


Figure 3. UV/vis spectra of oligomeric anilines in NMP. (A) as-synthesized tetramer; (B) as-synthesized octamer; (C) as-synthesized hexadecamer; (D) polyaniline EB, (all in emeraldine oxidation state)

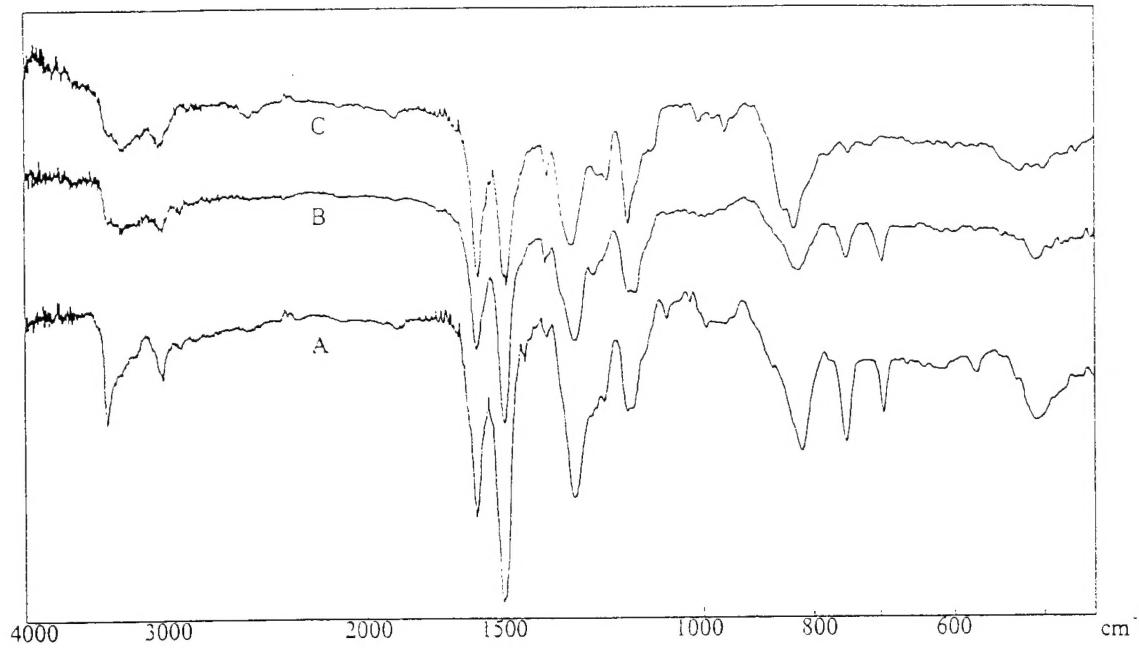


Figure 4. Diffuse reflectance FTIR spectra of oligomeric anilines. (A) as-synthesized tetramer; (B) as-synthesized hexadecamer; (C) polyaniline EB, (all in emeraldine oxidation state)

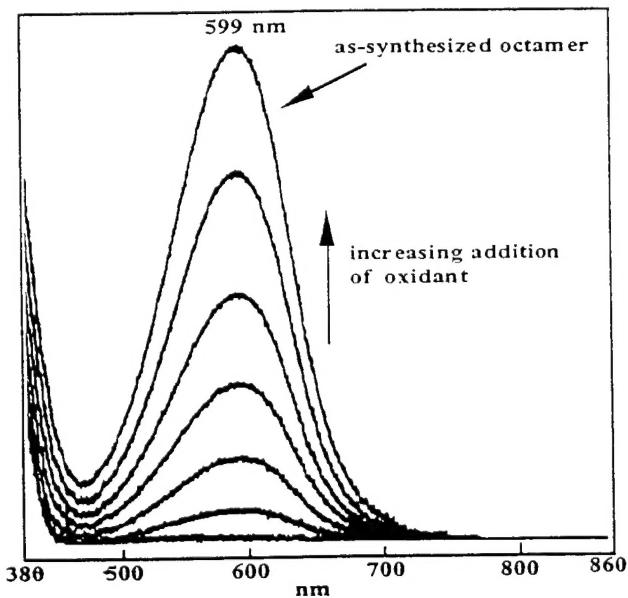


Figure 5. UV/Vis spectra of controlled oxidation of the leucoemeraldine oxidation state of the octamer with H_2O_2 in NMP.

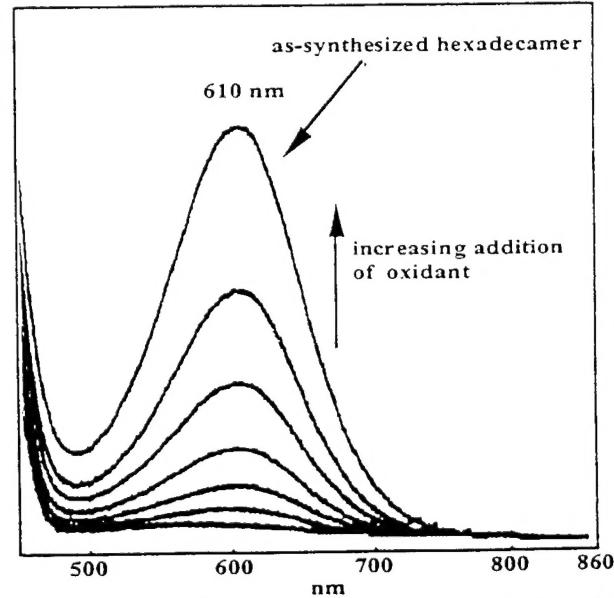


Figure 6. UV/Vis spectra of controlled oxidation of the leucoemeraldine oxidation state of the hexadecamer with H_2O_2 in NMP.